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(54) Title: PHOTSENSITIVE COMPOSITIONS CONTAINING COMB POLYMER BINDERS (57) Abstract <p>A novel class of comb polymer compositions are disclosed which are particularly useful in photosensitive formulations such as photoresists solder masks and the like. These compositions comprise a branched polymer product containing hydrophilic groups, i.e., comb polymer, comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment. The linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000 and the branch polymer segments have a weight average molecular weight (M_w) of about 40,000 or less, wherein the weight ratio of the backbone segment to the branch segments ranges between 200/1 to 1/4, and wherein the branch segments contain 35 % to 100 % of the hydrophilic groups. The comb polymers of this invention are particularly useful as binders in photosensitive compositions containing crosslinking monomers such as solder masks. Upon exposure to actinic radiation, solder mask coatings of such photosensitive compositions form permanent protective solder masks having superior toughness and flexibility.</p>		

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TITLEPHOTOSENSITIVE COMPOSITIONS CONTAINING
COMB POLYMER BINDERS

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CROSS REFERENCE TO RELATED APPLICATION

The present patent application is a continuation-in-part of copending patent application Serial No. 07/662,540 filed February 28, 1991.

10

BACKGROUND OF THE INVENTION

The present invention is directed to a novel composition of matter which is considered to be a type of comb polymer. The present invention also relates to liquid and solid imaging and photosensitive compositions containing such polymer products and including the use of such compositions as photoresists and solder masks.

Polymer products are used as components of imaging and photosensitive systems and particularly in photoimaging systems such as those described in "Light-Sensitive Systems: Chemistry and Application of Nonsilver Halide Photographic Processes" by J. Kosar, John Wiley & Sons, Inc., 1965 and more recently in "Imaging Processes And Materials - Neblette's Eighth Edition" Edited by J. Sturge, V. Walworth and A. Shepp, Van Nostrand Reinhold, 1989. In such systems, actinic radiation impinges on a material containing a photoactive component to induce a physical or chemical change in that material. A useful image or latent image which can be processed into a useful image can thereby be produced. Typically actinic radiation useful for imaging is light ranging from the near ultraviolet through the visible spectral regions, but in some

instances may also include infrared, deep-ultraviolet, X-ray and electron beam radiation.

Although the polymer product itself may be photoactive, generally a photosensitive composition
5 contains one or more photoactive components in addition to the polymer product. Upon exposure to actinic radiation, the photoactive component acts to change the rheological state, the solubility, the surface characteristics, refractive index, the color, the
10 electromagnetic characteristics or other such physical or chemical characteristics of the photosensitive composition as described in the Neblette's publication supra.

Polymer products are particularly useful in
15 photopolymerizable systems such as disclosed in Chapter 7 of the Neblette's publication supra. Such photopolymerizable systems typically have one or more linear polymers as a binding agent and at least one addition polymerizable monomeric component having one or
20 more sites of terminal ethylenic unsaturation. Frequently the binding agent is a simple polymer blend, i.e., an intimate mixture of two or more polymers wherein there is no covalent chemical bonding between the different species of polymer chains. During imaging
25 exposure, the monomeric component polymerizes and/or crosslinks to form a polymer or polymer network in which at least some of the polymeric binding agent is entrapped thereby photohardening or insolubilizing the exposed area.

30 Comb polymers are a particular class of branched polymers wherein multiple branch polymer segments are linked along a linear polymer backbone segment. Comb polymers may also be described as linear polymers with

polymeric arms. Such polymers typically are prepared by copolymerizing a conventional monomer with a macromer. Macromers are defined by Kawakami in the "Encyclopedia Of Polymer Science And Engineering", Vol. 9, pp. 195-204
5 (John Wiley & Sons, New York, 1987) to be polymers of molecular weight ranging from several hundred to tens of thousands, with a functional group at the end that can further polymerize, such as an ethylenic, an epoxy, a dicarboxylic acid, a diol or a diamino group. European
10 Patent Publication No. 280,979 discloses the use of such a polymer as a binding agent in a photopolymerizable material suitable for producing printing forms or resist patterns. The polymer binder disclosed consists of a film-forming copolymer that has a multi-phase morphology
15 where at least one phase has a glass transition temperature below room temperature and at least one other phase has a glass transition temperature above room temperature. The copolymer has an average molecular weight (weight average) of more than 10,000,
20 and is produced using an ethylenically unsaturated macromer with an average molecular weight (weight average) of 1000 to 100,000.

Although the physical and chemical properties of existing comb polymers are desirable in some
25 photosensitive systems, the branch polymer segments of the comb polymers used are highly polydisperse, typically have higher molecular weights and are relatively expensive to make. There is a need, which is not met by the current technology, to produce comb
30 polymer binders bearing hydrophilic functionality which have well defined structure, are less expensive to produce, and process well in photoimageable systems to produce tough, flexible, adherent or otherwise useful

polymer products, and to improve their end-use performance while reducing processing steps.

SUMMARY OF THE INVENTION

5 The present invention is directed to a branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the branch polymer product is formed
10 during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer, wherein

- 15 (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,
- (b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,
- 20 (c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and
- (d) the branch polymer segment(s) contain from
25 about 35% to 100% of the hydrophilic groups.

More particularly, the present invention is directed to a sensitive composition comprising the branched polymer product containing hydrophilic groups and at least one photoactive or thermally active
30 component. A specific embodiment of this invention is a sensitive composition comprising

- (a) a branched polymer product comprising a plurality of branch polymer segments

chemically linked along a linear polymer backbone segment wherein the branch polymer segments are formed during addition polymerization of the branched polymer product from at least one ethylenically unsaturated macromer component containing one or more hydrophilic functional groups, wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 30,000 and a polydispersity (M_w/M_n) of not greater than about 5, and (b) at least one photoactive or thermally active component.

15

DETAILED DESCRIPTION OF THE INVENTION

The sensitive compositions of this invention contains a novel branched polymer product, known as a comb polymer, having branch polymer segments, known as polymer arms, of limited molecular weight and limited weight ratio relative to the linear polymer backbone segment and which typically contains the majority of the hydrophilic groups present in the polymer product. The compositions likewise contain components, such as catalysts, photoinitiators and the like, which render the compositions reactive to thermal and/or radiant energy.

POLYMER PRODUCT

The branched polymer product contains hydrophilic groups and comprises one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment. The branch polymer product is formed during free radical addition polymerization of at least

one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer. The ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000 and the linear polymer backbone segment resulting from the polymerization has a weight average molecular weight (M_w) between about 10,000 and about 500,000. The weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and preferably within the range of about 80/20 to about 60/40. Preferably the macromer component has a weight average molecular weight (M_w) of several hundred to about 40,000 and more preferably of about 6,000 to about 15,000. Typically such ethylenically unsaturated macromer component can have a weight average molecular weight (M_w) equivalent to the molecular weight of 2 to about 500 monomer units used to form the macromer component and preferably between 30 and 200 monomeric units.

The branch polymer segments contain from about 35% to 100% by weight of the total hydrophilic groups present on the branch polymer product and preferably from about 50% to 100%. Preferred hydrophilic groups are protic groups such as hydroxy, amino, ammonium, amido, imido, urethano, ureido, or mercapto; or carboxylic, sulfonic, sulfinic, phosphoric, or phosphonic acids or salts thereof. Preferably, the hydrophilic groups are acid groups and particularly carboxylic acid groups, although other groups such as hydroxy may also be present. The acid containing branched polymer product of this invention, typically will contain between about 3% to about 20% by weight of acid groups and preferably between about 5% to about 10%. The branch polymer

segments of such an acid containing branched polymer product typically contain between 35% to 100% of the acid groups present. When the hydrophilic groups are acid groups, such a branch polymer product preferably has an acid number between about 20 and about 90, more preferably between about 40 and about 70, and the ethylenically unsaturated macromer component preferably has an acid number of about 50 and about 650, more preferably between about 90 and about 300.

Alternatively the branched polymer product may contain a basic group as the major fraction of the hydrophilic groups such as amine groups. In this instance, the ethylenically unsaturated macromer component preferably has an amine number between about 20 and about 90, more preferably between about 40 and about 70, and the ethylenically unsaturated macromer component preferably has an amine number of about 50 and about 650, more preferably between about 90 and about 300.

In a specific embodiment, the branched polymer product comprises a plurality of branch polymer segments chemically linked along a linear polymer backbone segment wherein the branch polymer segments have a weight average molecular weight (M_w) of about 30,000 and a polydispersity (M_w/M_n) of about 5 or less and have at least one hydrophilic group bonded thereto. Polydispersity is employed in its conventional sense as the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n), i.e., M_w/M_n .

The branched polymer product of this invention is a copolymer of at least one ethylenically unsaturated macromer component having one or more hydrophilic functional groups bonded thereto. Generally the overall

polymer molecular weight will be up to about 500,000, although higher molecular weights are possible.

The branched polymer product contains at least 0.5% by weight of branch linear segments. The branch linear segments, also known as polymer arms, typically are uniformly distributed along the linear polymer backbone segment. The "polymer arm" or branch polymer segment is a polymer or oligomer of at least two repeating monomer units, which is attached to the linear polymer by a covalent bond. The branch polymer segment, or polymer arm, is incorporated into the branched polymer product as a macromer component, during the addition polymerization process of a macromer and a comonomer. A "macromer" for the purpose of this invention, is a polymer, copolymer or oligomer of molecular weight ranging from several hundred to about 40,000 containing a terminal ethylenically unsaturated polymerizable group. Preferably the macromer is a linear polymer or copolymer end capped with an ethylenic group. Typically, the branched polymer product is a copolymer bearing one or more polymer arms, and preferably at least two polymer arms, and is characterized in that between about 0.5 and about 80 weight % of the monomeric components used in the polymerization process is a macromer. Typically, comonomer components used along with the macromer in the polymerization process likewise contain a single ethylenic group that can copolymerize with the ethylenically unsaturated macromer.

The ethylenically unsaturated macromer and the resulting branch polymer segment of the branched polymer product has bonded thereto one or more hydrophilic functional groups. For the purposes of this invention, a "hydrophilic group" is intended to mean a functional

group which enhances the solubility, swellability, or dispersibility in aqueous environments, of the macromer and/or the branched polymer product to which it is bonded. Preferred hydrophilic groups are protic functional groups such as hydroxy, carboxylic, amino, ammonium, amide, imide, urethane, ureido, sulfonic, sulfinic, phosphoric, phosphonic, mercaptan, or salts thereof. The functional group may be incorporated into the ethylenically unsaturated macromer either during or after its formation, but typically before formation of the branched polymer product.

The branched polymer segments attached to the linear polymer backbone segment can be any of those derived from ethylenically unsaturated macromers prepared according to the general descriptions in U.S. Patent 4,680,352 and U.S. Patent 4,694,054 which are incorporated herein by reference. Macromers are prepared by free radical polymerization processes employing a cobalt compound as a catalytic chain transfer agent and particularly a cobalt(II) compound. The cobalt(II) compound may be a pentacyanocobalt(II) compound or a cobalt(II) chelate of a vicinal iminohydroxyimino compound, a dihydroxyimino compound, a diazadihydroxyimninodialkyldecadiene, a diazadihydroxyimninodialkylundecadiene, a tetraaza-tetraalkylcyclotetradecatetraene, a tetraaza-tetraalkylcyclododecatetraene, a bis(difluoroboryl) diphenyl glyoximato, a bis(difluoroboryl) dimethyl glyoximato, a N,N'-bis(salicylidene)ethylenediamine, a dialkyldiaza-dioxodialkyldecadiene, or a dialkyldiazadioxodialkyl-tridecadiene. Low molecular weight methacrylate macromers may also be prepared with a pentacyanocobalt(II) catalytic chain transfer agent as

disclosed in U.S. Patent 4,722,984 which is incorporated herein by reference.

Illustrative macromers are vinyl polymers, acrylic polymers and copolymers of acrylic monomers and vinyl monomers wherein the polymers or copolymers have a terminal ethylenic group and a hydrophilic functional group. Preferred monomer components for use in preparing macromers include: methyl methacrylate (MMA); ethyl methacrylate (EMA); butyl methacrylate (BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl acrylate (EA); butyl acrylate (BA); 2-ethylhexyl acrylate; 2-hydroxyethyl methacrylate (HEMA); 2-hydroxyethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); esters of acrylic and methacrylic acid wherein the ester group contains from 1 to 18 carbon atoms; nitriles and amides of acrylic and methacrylic acid; glycidyl methacrylate and acrylate; itaconic acid (IA) and itaconic acid anhydride, half ester and imide; maleic acid and maleic acid anhydride, half ester and imide; aminoethyl methacrylate; t-butyl aminoethyl methacrylate; dimethyl aminoethyl methacrylate; diethyl aminoethyl methacrylate; aminoethyl acrylate; dimethyl aminoethyl acrylate; diethyl aminoethyl acrylate; acrylamide; N-t-octyl acrylamide; vinyl methyl ether; styrene (S); alpha-methyl styrene; vinyl acetate; vinyl chloride; and the like.

In contrast to comb polymers of the prior art, the branched polymer segments of the branched polymer product of this invention have limited molecular weight, polydispersity, and hydrophilicity as determined by the macromer component from which the branched polymer product is made.

Macromers useful in this invention have limited molecular weight and may have limited polydispersity. Preferably the macromer will have a weight average molecular weight (M_w) of about 40,000 to several hundred. In a specific embodiment, the macromer has a polydispersity (M_w/M_n) of about 5 or less. The lower molecular weight limit of the macromer will be equivalent to the molecular weight of two, three or four monomer units used to form the macromer. Preferably the macromer component has a weight average molecular weight (M_w) equivalent to the molecular weight of 2 to about 500 monomer units used to form the macromer component, and preferably between 30 and 200 monomer units. Typically the macromer component comprises between about 0.5 and about 80 weight % of the components used to prepare the branched polymer product and preferably between about 5 and about 50 weight %.

The branched polymer product may be prepared by any conventional addition polymerization process. The branched polymer product, or comb polymer, may be prepared from one or more compatible ethylenically unsaturated macromer components and one or more compatible, conventional ethylenically unsaturated comonomer component(s). Preferred addition polymerizable, ethylenically unsaturated comonomer components include: methyl methacrylate (MMA); ethyl methacrylate (EMA); butyl methacrylate (BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl acrylate (EA); butyl acrylate (BA); 2-ethylhexyl acrylate; 2-hydroxyethyl methacrylate (HEMA); 2-hydroxyethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); itaconic acid (IA) and itaconic acid anhydride, half ester and imide; maleic acid and maleic

acid anhydride, half ester and imide; aminoethyl methacrylate; t-butyl aminoethyl methacrylate; dimethyl aminoethyl methacrylate; diethyl aminoethyl methacrylate; aminoethyl acrylate; dimethyl aminoethyl acrylate; diethyl aminoethyl acrylate; acrylamide; N-t-octyl acrylamide; vinyl methyl ether; styrene (S); alpha-methyl styrene; vinyl acetate; vinyl chloride; and the like.

Each constituent linear polymer backbone segment and/or branch polymer segment of the branched polymer product of this invention may contain a variety of functional groups inclusive of the hydrophilic functional groups described supra. A "functional group" is considered to be any moiety capable of being attached to a polymer or branch polymer segment by a direct valence bond or by a linking group. Illustrative of functional groups which can be borne by the polymer backbone segment or the branch polymer segments are -COOR; -OR; -SR (where R can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl, a heterocyclic, or -OR₁ where R₁ can be alkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); -CN; -NR₂R₃ or $\overset{\text{O}}{\parallel}\text{-C-NR}_2\text{R}_3$ (where R₂ and R₃ can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl, aralkyl, -CH₂OR₄ (where R₄ is hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl, aralkyl), or together R₂ and R₃ can form a heterocyclic ring); $\overset{\text{R}_5}{\underset{|}{\text{-C}}}=\text{CR}_6\text{R}_7$ (where R₅, R₆ and R₇ can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl, aralkyl, or -COOR or when taken together R₅, R₆ and/or R₇ can form a cyclic group); -SO₃H; a urethane group; an isocyanate or blocked isocyanate group; a urea group; an

oxirane group; an aziridine group; a quinone diazide group; an azo group; an azide group; a diazonium group; an acetylacetoxy group; $-\text{SiR}_8\text{R}_9\text{R}_{10}$ (where R_8 , R_9 and R_{10} can be alkyl or cycloalkyl of 1-12 carbon atoms or $-\text{OR}_{11}$ where R_{11} is alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); or an $-\text{OSO}_3\text{R}_{12}$, $-\text{OPO}_2\text{R}_{12}$, $-\text{PO}_2\text{R}_{12}$, $-\text{PR}_{12}\text{R}_{13}\text{R}_{14}$, $-\text{OPOR}_{12}$, $-\text{SR}_{12}\text{R}_{13}$, or $-\text{N}^+\text{R}_{12}\text{R}_{13}\text{R}_{14}$ group (where R_{12} , R_{13} and R_{14} can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); or a salt or onium salt of any of the foregoing. Preferred functional groups are $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, an amide group, a vinyl group, a urethane group, an isocyanate group, a blocked isocyanate group or combinations thereof.

Functional groups may be located anywhere on the branch polymer product. However, it is sometimes desirable to choose comonomers which impart bulk polymer characteristics to the linear polymer backbone segment of the polymer product and macromers which impart physical and chemical functionality to the branch polymer segments in addition to hydrophilicity, such as solubility, reactivity, and the like.

This invention also relates to dispersions, solvent and melt solutions, coatings and molded articles of a branched polymer product comprising a plurality of branch polymer segments chemically linked along a single linear polymer backbone segment wherein the branch polymer segments are formed during addition polymerization of the branched polymer product from at least one ethylenically unsaturated macromer component containing one or more hydrophilic functional groups, wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not

greater than about 40,000. Polydispersity (M_w/M_n) may be not greater than about 5. This invention particularly relates to such dispersions which are sensitive and which additionally contain at least one
5 photoactive or thermally active component.

The dispersions or solutions of the polymer product can be used, with or without pigments, to make coatings for industrial, cosmetic and automotive purposes. They are especially useful for applying mar-resistant
10 finishes to automobile and truck parts, for coating plastic automobile parts and as pigment dispersants. The dispersions or solutions are also useful as finger-nail polish or other such cosmetic coatings or materials.

15 The residues from removal of the organic liquids from the dispersions or solutions can be used to make films useful as semi-permeable membranes for the purification of water and for use in electrolytic cells, as mar-resistant tough films for structural automobile
20 parts and building panels, as mold release films, as adhesive films, e.g., for the manufacture of multilayer printed circuits, as photoresists and as solder masks and for the formation of curved panels of various plastic materials in aircraft and automobile production.
25 The branched polymer products can also be extruded or molded into various useful shapes, can be used as elastomers, can be used in the fabrication of gaskets, hoses, belts and bushings, and as adhesives.

Superior toughness-flexibility balance and solvent
30 resistance can be built into the branched polymer products by crosslinking one or more of the polymer constituents with such crosslinking agents as epoxies, isocyanates and aminoplast resins.

SENSITIVE COMPOSITIONS

The branched polymer products are particularly useful in sensitive compositions containing at least one

5 photoactive or thermally active component and in particular in photosensitive compositions such as photoresists, solder masks, and the like, which will be further described to illustrate this invention.

"Photoactive", which is synonymous with

- 10 "photosensitive", describes a material which changes its chemical or physical nature, or causes such a change, upon exposure to actinic radiation, in such a way that the change is formed directly, e.g., an image, or that a precursor, e.g., a latent image, is formed which upon
- 15 further treatment produces the desired change.

"Thermally active" describes a material which changes its chemical or physical nature, or causes such a change, when its temperature is raised or when a substance is added or removed. Illustrative of such a

- 20 photoactive or thermally active component is a material which cyclizes, dimerizes, polymerizes, crosslinks, generates a free radical, generates an ionic species or dissociates upon exposure to actinic radiation or when it is heated. Photoactive or photosensitive component
- 25 includes a photoinitiator, a photosensitizer or a combination thereof; a photosolubilizer; a photodesensitizer; a photoinhibitor; a phototackifier; a photodetackifier; or a component which is photodegradable; photochromic; photoreducible; photo-
- 30 oxidizable; photoadhesive; photoreleaseable; photomagnetic; photodemagnetic; photoconductive or photoinsulative; or is a material which changes or causes changes in refractive index upon exposure to

actinic radiation. The sensitive compositions of this invention include those instances in which component (b) is bonded to component (a); or in which component (b) comprises:

- 5 (i) a polymerizable monomer, and
- (ii) an initiating system activatable by actinic radiation.

The branched polymer products are useful as components of photosensitive systems and particularly in
10 photoimaging systems such as those described in "Light-Sensitive Systems: Chemistry and Application of Nonsilver Halide Photographic Processes" by J. Kosar, John Wiley & Sons, Inc., 1965 and more recently in
"Imaging Processes And Materials - Neblette's Eighth
15 Edition" Edited by J. Sturge, V. Walworth and A. Shepp, Van Nostrand Reinhold, 1989. In such systems, actinic radiation impinges on a material containing a photoactive component to induce a physical or chemical change in that material. A useful image or latent image
20 which can be processed into a useful image can thereby produced. Typically actinic radiation useful for imaging is light ranging from the near ultraviolet through the visible spectral regions, but in some instances may also include infrared, deep-ultraviolet,
25 X-ray and electron beam radiation.

Although the branched polymer product itself may be photoactive, generally a photosensitive composition contains one or more photoactive components in addition to the branched polymer product. Upon exposure to
30 actinic radiation, the photoactive component acts to change the rheological state, the solubility, the surface characteristics, refractive index, the color, the electromagnetic characteristics or other such

physical or chemical characteristics of the photosensitive composition as described in the Neblette's publication supra.

Typically the photosensitive compositions of this invention are used in the form of a supported film or layer although unsupported solid objects may also be prepared. The photosensitive composition is applied to a suitable substrate to form a continuous film or layer thereon which is imagewise exposed to actinic radiation to form an image directly or latent image.

Alternatively, the layer may be uniformly exposed to actinic radiation to cure or harden the layer when the photosensitive composition is applied either in the form of a continuous or patterned layer such as a protective finish, a paint or ink. Any conventional source of actinic radiation may be used including arc, discharge, and incandescent lamps as well as lasers, X-ray and electron beam units. The layer may be applied as a neat, solvent-free, photosensitive liquid or as a solution and dried to a solid layer wherein any conventional coating or printing process may be used. Alternatively, the layer or film may be applied by laminating a supported solid photosensitive layer to the substrate and then optionally removing the support.

Applications requiring no additional processing steps after exposure to actinic radiation, include those where an image is formed directly, e.g., photopolymer holograms as disclosed in Haugh U.S. Patent 3,658,526 wherein the refractive index changes upon exposure to actinic radiation, diffusion resists as in Gervay and Walker U.S. Patent 3,718,473, color forming systems as in Cescon and Dessauer U.S. Patent 3,445,234 or other photochromic systems. Color forming systems based on

photooxidatizable or photoreducible agents are disclosed in MacLachlan U.S. Patent 3,390,996. Also included are those applications where decorative or protective coatings are applied and photocured or where a patterned layer is applied and photocured, e.g., a photoresist screen printing ink as in Lipson et al. U.S. Patent 4,003,877.

In those instances when a latent image is formed, the exposed or unexposed areas of the layer containing the latent image are then modified by removing exposed or unexposed areas, depositing a material on or in the exposed or unexposed areas or further treating the layer to develop an imaged layer. Exposed or unexposed areas of the layer may be removed to form either a deep relief image or a thin stencil image with solvent or aqueous alkaline developers therefor or they may be peeled from the complimentary unexposed or exposed areas adhered to the substrate. A deep relief image in which the sides of the relief are tapered and do not extend to the substrate, typically is used as a letterpress or flexographic printing plate, e.g., as disclosed in Plambeck U.S. Patent 2,760,863 and Brennen and Chen U.S. Patent 4,323,637. A stencil image, in contrast, is a thin relief having vertical side walls down to the substrate thereby forming complimentary uncovered substrate surface areas. A stencil image has numerous applications, e.g., as a resist as disclosed in Celeste U.S. Patent 3,469,982, as a lithographic printing plate as in Alles U.S. Patent 3,458,311, a photopolymer litho film as in Bratt and Cohen U.S. Patent 4,229,517, a peel-apart drafting film as in Colgrove U.S. Patent 3,353,955, or in peel-apart proofing systems as in Cohen and Fan U.S. Patent 4,247,619. When a stencil image is

formed and is used as a resist, unprotected substrate areas are formed which may be further modified by etching the unprotected surface areas or depositing a material thereon. The exposed or unexposed areas of the layer containing the latent image may be modified by depositing a material thereon such as a photodetackification process wherein powdered material is adhered to the unexposed areas, e.g., as in the proofing process of Chu and Cohen U.S. Patent 3,649,268, or a phototackification or photoadhesive process where powdered material is adhered to the exposed areas of the layer, e.g., as in the proofing processes of Chu et al. U.S. Patent 4,243,741 and Grossa U.S. Patent 4,604,340. Liquid toners are also used in electrostatic systems to develop latent images in a photoconductive or a photoinsulative process such as disclosed in Riesenfeld et al. U.S. Patent 4,732,831. Photomagnetic and photodemagnetic systems are used to apply dye to fabrics and resists to circuit boards as disclosed in Gorondy U.S. Patent 4,105,572, Nacci U.S. Patent 4,292,120 and Nacci et al. U.S. Patents 4,338,391 and 4,359,516. Photosensitive compositions containing a latent image may also be developed into an image by treatment with a reagent or by further treatment with actinic radiation or heat. Conventional silver halide or diazotype systems form a latent image upon exposure which is developed into a visible image upon treatment with a developing reagent. In some silver halide direct-writing systems, development to a visible image is accomplished by uniform exposure to actinic radiation. In some reversal imaging processes the treatment step is used to complete the formation of the latent image before or during development. Such systems include

photopolymer systems, e.g., as disclosed in Pazos U.S. Patent 4,198,242 or Dueber et al. U.S. Patent 4,477,556, containing a photoinhibitor wherein imaging exposure generates inhibitor in the exposed areas of the layer and a subsequent uniform exposure to actinic radiation, or in some instances uniformly heated, generates a latent image in the complimentary areas free of photogenerated inhibitor. Such reversal systems also include photodesensitizable systems, e.g., as disclosed in Roos U.S. Patent 3,778,270, wherein, in the exposed areas, a component required for image or latent image formation is degraded or desensitized to an inactive form and the component in the unexposed areas is developed into an image or latent image by subsequent treatment with a reagent.

Illustrative of such photosensitive systems are those described in Chapter 7, "Polymer Imaging" by A. B. Cohen and P. Walker in Neblette's supra, pages 226-262, in which photocrosslinking, photodimerization, photocyclization, photosolubilization, and both ionic and free radical photopolymerization, as well as electrostatic photopolymer imaging and solid imaging are discussed. In Chapter 8, "Low Amplification Imaging Systems" by R. Dessauer and C. E. Looney, pages 263-278, imaging systems discussed include color forming free radical, diazo, and vesicular systems, photochromism, phototackification and photodetackification as well as thermal and photothermal systems.

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PHOTOPOLYMERIZABLE COMPOSITIONS

The branched polymer products are particularly useful in photopolymerizable compositions which contains a monomeric material and a photoinitiator system. In

such systems the branched polymer product functions as a dispersible polymeric binder component to impart desired physical and chemical characteristics to the exposed and unexposed photopolymerizable composition. Upon exposure to actinic radiation, the photoinitiator system induces chain propagated polymerization of the monomeric material by either a condensation mechanism or by free radical addition polymerization. While all photopolymerizable mechanisms are contemplated, the compositions and processes of this invention will be described in the context of free radical initiated addition polymerization of monomers having one or more terminal ethylenically unsaturated groups. In this context, the photoinitiator system when exposed to actinic radiation acts as a source of free radicals needed to initiate polymerization of the monomer. The photoinitiator of the system may be activated by a photosensitizer which absorbs actinic radiation which may be outside the absorption spectrum of the initiator itself, to sensitize the addition polymerization in more practical radiation spectral regions such as near ultraviolet, visible light and near infrared. In the narrow sense, the term photoactive component of the compositions of this invention refers to the material which absorbs the actinic radiation, e.g., the photoinitiator or the photosensitizer, but in the broader sense the term photoactive component refers to any or all the essential materials needed for photopolymerization, i.e., the photoinitiating system and the monomer.

Photopolymerizable compositions contain the branched polymer products, an initiating system activated by actinic radiation, and at least one

nongaseous ethylenically unsaturated compound having a boiling point above 100°C at normal atmospheric pressure and being capable of forming a high polymer by photoinitiated addition polymerization. Preferred
5 photopolymerizable compositions contain mono or polyfunctional acrylates or methacrylates and particularly preferred are such compositions containing monomers with two, three or more acrylate or methacrylate groups to allow concurrent crosslinking
10 during the photopolymerization process.

ADDITION POLYMERIZABLE MONOMERS

Suitable monomers which can be used as the sole monomer or in combination with others include the
15 following: t-butyl acrylate, 1,5-pentanediol diacrylate, N,N-diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-propanediol diacrylate, decamethylene glycol diacrylate,
20 decamethylene glycol dimethacrylate, 1,4-cyclohexanediol diacrylate, 2,2-dimethylolpropane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyoxyethylated
25 trimethylolpropane triacrylate and trimethacrylate and similar compounds as disclosed in U.S. Patent 3,380,831, 2,2-di(p-hydroxyphenyl)-propane diacrylate, pentaerythritol tetraacrylate, 2,2-di-(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate,
30 polyoxyethyl-2,2-di-(p-hydroxyphenyl)-propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloxyethyl) ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl) ether of

- bisphenol-A, di-(2-acryloxyethyl) ether of bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of tetrachloro-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrachloro-bisphenol-A, di-(3-methacryloxy-2-
- 5 hydroxypropyl) ether of tetrabromo-bisphenol-A, di-(2-methacryloxyethyl) ether of tetrabromo-bisphenol-A, di-(3-methacryloxy-2-hydroxypropyl) ether of 1,4-butanediol, di-(3-methacryloxy-2-hydroxypropyl) ether of diphenolic acid, triethylene glycol dimethacrylate,
- 10 polyoxypropyl one trimethylol propane triacrylate (462), ethylene glycol dimethacrylate, butylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, 2,2,4-trimethyl-1,3-pentanediol dimethacrylate, pentaerythritol
- 15 trimethacrylate, 1-phenyl ethylene-1,2-dimethacrylate, pentaerythritol tetramethacrylate, trimethylol propane trimethacrylate, 1,5-pentanediol dimethacrylate, diallyl fumarate, styrene, 1,4-benzenediol dimethacrylate, 1,4-diisopropenyl benzene, and 1,3,5-triisopropenyl benzene.
- 20 A class of monomers are an alkylene or a polyalkylene glycol diacrylate prepared from an alkylene glycol of 2 to 15 carbons or a polyalkylene ether glycol of 1 to 10 ether linkages, and those disclosed in U.S. Patent 2,927,022, e.g., those having a plurality of
- 25 addition polymerizable ethylenic linkages particularly when present as terminal linkages. Preferred are those wherein at least one and preferably most of such linkages are conjugated with a double bonded carbon, including carbon double bonded to carbon and to such
- 30 heteroatoms as nitrogen, oxygen and sulfur. Also preferred are such materials wherein the ethylenically unsaturated groups, especially the vinylidene groups, are conjugated with ester or amide structures.

A particularly preferred class of monomers are t-butyl acrylate, cyclohexyl acrylate, hydroxy C1-C10-alkyl acrylate, butane diol diacrylate, hexamethylene glycol diacrylate, triethylene glycol diacrylate, tripropylene glycol diacrylate, pentaerythritol triacrylate, trimethylolpropane triacrylate, polyoxyethylated trimethylolpropane triacrylate, di-(3-acryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(3-acryloxy-2-hydroxypropyl) ether of tetrabromo-bisphenol-A, or methacrylate analogues thereof.

PHOTOINITIATOR SYSTEMS

The photoinitiator system has one or more compounds that directly furnish free-radicals when activated by actinic radiation. The system also may contain a sensitizer that is activated by the actinic radiation, causing the compound to furnish the free-radicals. Useful photoinitiator systems typically will contain a sensitizer that extends spectral response into the near ultraviolet, visible, and near infrared spectral regions.

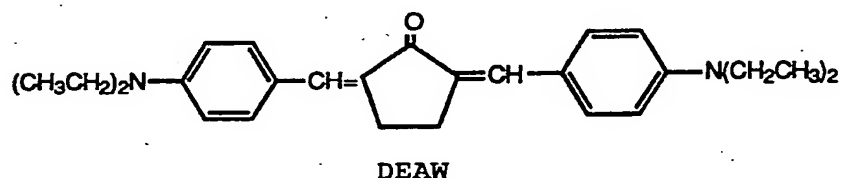
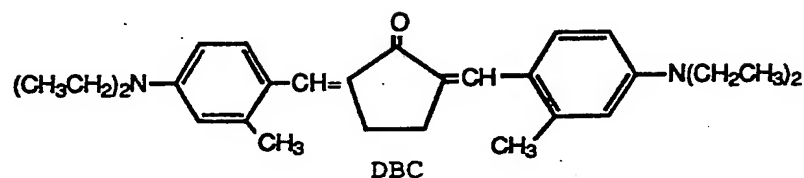
A large number of free-radical generating compounds, including redox systems such as Rose Bengal/2-dibutylaminethanol, may be selected to advantage. Photoreducible dyes and reducing agents such as those disclosed in U.S. Patents: 2,850,445; 2,875,047; 3,097,096; 3,074,974; 3,097,097; 3,145,104; and 3,579,339; as well as dyes of the phenazine, oxazine, and quinone classes; ketones, quinones; 2,4,5-triphenylimidazolyl dimers with hydrogen donors, and mixtures thereof as described in U.S. Patents; 3,427,161; 3,479,185; 3,549,367; 4,311,783; 4,622,286; and 3,784,557 can be used as initiators. Other

initiators are dye-borate complexes disclosed in U.S. Patent 4,772,541; and trichloromethyl triazines disclosed in U.S. Patents 4,772,534 and 4,774,163. A useful discussion of dye sensitized photopolymerization can be found in "Dye Sensitized Photopolymerization" by D. F. Eaton in Adv. in Photochemistry, Vol. 13, D. H. Volman, G. S. Hammond, and K. Gollinick, eds., Wiley-Interscience, New York, 1986, pp. 427-487. Similarly, the cyclohexadienone compounds of U.S. Patent No. 4,341,860 are useful as initiators.

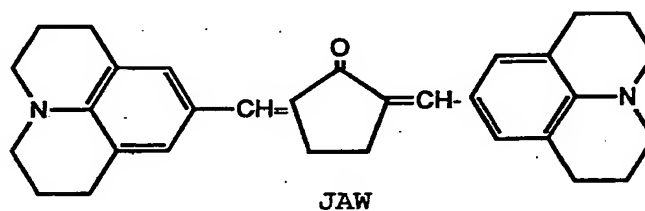
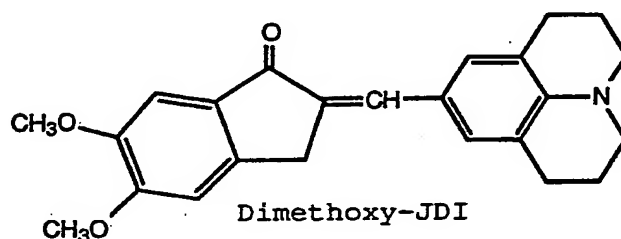
Preferred photoinitiators include CDM-HABI, i.e., 2-(o-chlorophenyl)-4,5-bis(m-methoxyphenyl)-imidazole dimer; o-Cl-HABI, i.e., 1,1'-biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenyl-; and TCTM-HABI, i.e., 1H-imidazole, 2,5-bis(o-chlorophenyl)-4-[3,4-dimethoxyphenyl]-, dimer, each of which is typically used with a hydrogen donor.

Sensitizers useful with photoinitiators include methylene blue and those disclosed in U.S. Patents 3,554,753; 3,563,750; 3,563,751, 3,647,467; 3,652,275; 4,162,162; 4,268,667; 4,351,893; 4,454,218; 4,535,052; and 4,565,769. A preferred group of sensitizers include the bis(p-dialkylaminobenzylidene) ketones disclosed in Baum et al. U.S. Patent 3,652,275, and the arylidene aryl ketones disclosed in Dueber U.S. Patent 4,162,162. Preferred sensitizers include the following: DBC, i.e., cyclopentanone; 2,5-bis-{[4-(diethylamino)-2-methylphenyl]-methylene}; DEAW, i.e., cyclopentanone, 2,5-bis{[4-(diethylamino)-phenyl]methylene}; dimethoxy-JDI, i.e., 1H-inden-1-one, 2,3-dihydro-5,6-dimethoxy-2-[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]-quinolizin-9-yl)methylene]-; and JAW, i.e., cyclopentanone, 2,5-bis[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-1-

yl)methylene]; which have the following structures respectively:



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10 Other particularly useful sensitizers are cyclopentanone, 2,5-bis[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene) ethylidene], CAS 27713-85-5; and cyclopentanone, 2,5-bis[2-(1-ethylnaphtho[1,2-d]thiazol-2(1H)-ylidene)ethylidene], CAS 27714-25-6.

15 Hydrogen donor compounds that function as chain transfer agents in the photopolymer compositions

include: 2-mercaptobenzoxazole, 2-mercaptobenzothiazole, 4-methyl-4H-1,2,4-triazole-3-thiol, etc.; as well as various types of compounds, e.g., (a) ethers, (b) esters, (c) alcohols, (d) compounds containing allylic or benzylic hydrogen, (e) acetals, (f) aldehydes, and (g) amides disclosed in column 12, lines 18 to 58 of MacLachlan U.S. Patent 3,390,996. Suitable hydrogen donor compounds for use in systems containing both biimidazole type initiator and N-vinyl carbazole are 5-chloro-2-mercaptobenzothiazole; 2-mercaptobenzothiazole; 1H-1,2,4-triazole-3-thiol; 6-ethoxy-2-mercaptobenzothiazole; 4-methyl-4H-1,2,4-triazole-3-thiol; 1-dodecanethiol; and mixtures thereof. A particularly preferred class of photoinitiators and photosensitizers are benzophenone, Michler's ketone, ethyl Michler's ketone, p-dialkylaminobenzaldehydes, p-dialkylaminobenzoate alkyl esters, polynuclear quinones, thioxanthenes, hexaarylbiimidazoles, cyclohexadienones, benzoin, benzoin dialkyl ethers, or combinations thereof where alkyl contains 1 to 4 carbon atoms.

OPTIONAL COMPONENTS

Other compounds conventionally added to photopolymer compositions can also be present to modify the physical properties of the film for a particular use. Such components include: other polymeric binders, fillers, thermal stabilizers, hydrogen donors, thermal crosslinking agents, optical brighteners, ultraviolet radiation materials, adhesion modifiers, coating aids, and release agents.

CROSSLINKING AGENTS

When the photopolymerizable composition is to be used as a permanent coating, such as a solder mask, a chemically or thermally activated crosslinking agent may be incorporated to improve high temperature characteristics, chemical resistance or other mechanical or chemical properties required in the end-use product. Suitable crosslinking agents include those disclosed in Gervay U.S. Patent 4,621,043 and Geissler et al. U.S. Patent 4,438,189, such as melamines, ureas, benzoguanamines and the like.

Examples of suitable crosslinking compounds include: N-Methylol compounds of organic carboxamides such as N,N'-dimethylolurea, N,N'-dimethyloloxamide, N,N'-dimethylolmalonamide, N,N'-dimethylolsuccinimide, N,N'-dimethylolsebacamide, N,N',N"-trimethylolcitramide, 1,3-dimethylolimidazolidine-2-one, 1,3-dimethylol-4,5-dihydroxyimidazidine-2-one, 1,3-dimethylolperhydropyrimidine-2-one, trimethylolmelamine, tetramethylolmelamine, hexamethylolmelamine, 1,3-dimethylol-5-methylperhydro-1,3,5-triazine-2-one, 1,3-dimethylol-5-allylperhydro-1,3,5-triazine-2-one, 1,3-dimethylol-5-butylperhydro-1,3,5-triazine-2-one, 1,2-bis-[1,3-dimethylolperhydro-1,3,5-triazine-2-one-5-yl]ethane, tetramethylolhydrazine dicarboxamide, N,N'-dimethylolterephthalamide, N,N'-dimethylolbenzene-1,3-disulfonamide and tetramethylolglycoluril; and C-methylol compounds of phenols, phenol-ethers and aromatic hydrocarbons 2,4,6-trimethylolphenol, 2,6-dimethylol-4-methylanisole, 2,6-dimethylol-4-methylphenol, 1,3-dimethylol-4,6-diisopropylbenzene, 2,2-bis-(4-hydroxy-3,5-dimethylolphenyl)propane, and 3,3'-dimethylol-4,4'-dihydroxydiphenyl sulfone.

Instead of the aforementioned methylol compounds, it is also possible to use, for example, the corresponding methyl, ethyl or butyl ethers, or esters of acetic acid or propionic acid. Suitable examples include: 4,4'-bismethoxymethyldiphenyl ether, tris-methoxymethyl-diphenyl ether, tetrakis-methoxymethylhydrazinedicarboxamide, tetrakis-methoxymethylglycoluril, tetrakis-hydroxyethoxymethylglycoluril, bis-acetoxymethyldiphenyl ether, hexamethoxymethyl-melamine. A preferred crosslinking agent of this class is hexamethoxymethyl melamine.

Also useful as crosslinking agents are compounds containing two or more epoxy groups such as the bis-epoxides disclosed in Herwig et al. U.S. Patent 4,485,166. Suitable bis-epoxides include bis-glycidal ethers of dihydric alcohols and phenols such as bisphenol A, of polyethylene glycol and polypropylene glycol ethers of bisphenol A, of butane-1,4-diol, hexane-1,6-diol, polyethylene glycol, propylene glycol or polytetrahydrofuran. Bis-glycidyl ethers of trihydric alcohols, such as glycerol, or of halogenated bisphenol A, such as tetra-bromo bisphenol A, can also be used. Preferred crosslinking agents of this class are 2,2-bis-(4-glycidoxy-phenyl)-propane, 2,2-bis-(4-epoxyethoxy-phenyl)-propane, bis-glycidyl ether of tetra-chloro-bisphenol A, bis-glycidyl ether of tetra-bromo-bisphenol A, bis-oxiranyl ether of tetra-chloro-bisphenol A, and bis-oxiranyl ether of tetra-bromo-bisphenol A.

Also useful as crosslinking agents are blocked polyisocyanates. Upon heating the blocked polyisocyanate, the blocking groups split off to yield the free reactive polyisocyanate. Useful

polyisocyanates include toluene diisocyanate; isophorone diisocyanate; 1,4-naphthalene diisocyanate; 1,6-hexamethylene diisocyanate; tetramethyl xylene diisocyanate; bis(4-isocyanatocyclohexyl)methane and the like. Useful blocking groups are derived from caprolactam; diethyl malonate; alcohols; phenols; oximes, e.g., methyl ethyl ketoxime; and the like.

POLYMERIC MODIFIERS

10 The photopolymerizable composition may contain a second polymeric binder to modify adhesion, flexibility, hardness, oxygen permeability, moisture sensitivity and other mechanical or chemical properties required during its processing or end use. Suitable polymeric binders
15 which can be used in combination with the branched polymer product of this invention include:
 Polyacrylate and alpha-alkyl polyacrylate esters, e.g., polymethyl methacrylate and polyethyl methacrylate; polyvinyl esters, e.g., polyvinyl acetate,
20 polyvinyl acetate/acrylate, polyvinyl acetate/methacrylate and hydrolyzed polyvinyl acetate; ethylene/vinyl acetate copolymers; polystyrene polymers and copolymers, e.g., with maleic anhydride and esters; vinylidene chloride copolymers, e.g., vinylidene
25 chloride/acrylonitrile; vinylidene chloride/methacrylate and vinylidene chloride/vinyl acetate copolymers; polyvinyl chloride and copolymers, e.g., poly(vinyl chloride/vinyl acetate); polyvinyl pyrrolidone and copolymers, e.g., poly(vinyl
30 pyrrolidone/vinyl acetate) saturated and unsaturated polyurethanes; synthetic rubbers, e.g., butadiene/acrylonitrile, acrylonitrile/butadiene/styrene,

- methacrylate/acrylonitrile/butadiene/styrene copolymers, 2-chlorobutadiene-1,3 polymers, chlorinated rubber, and styrene/butadiene/styrene, styrene/isoprene/styrene block copolymers; high molecular weight polyethylene
- 5 oxides of polyglycols having average molecular weights from about 4,000 to 1,000,000; epoxides, copolyesters, e.g., those prepared from the reaction product of a polymethylene glycol of the formula $\text{HO}(\text{CH}_2)_n\text{OH}$, where n is a whole number 2 to 10 inclusive, and (1)
- 10 hexahydroterephthalic, sebacic and terephthalic acids, (2) terephthalic, isophthalic and sebacic acids, (3) terephthalic and sebacic acids, (4) terephthalic and isophthalic acids, and (5) mixtures of copolyesters prepared from said glycols and (i) terephthalic,
- 15 isophthalic and sebacic acids and (ii) terephthalic, isophthalic, sebacic and adipic acid; nylons or polyamides, e.g., N-methoxymethyl polyhexamethylene adipamide; cellulose esters, e.g., cellulose acetate, cellulose acetate succinate and cellulose acetate
- 20 butyrate; cellulose ethers, e.g., methyl cellulose, ethyl cellulose and benzyl cellulose; polycarbonates; polyvinyl acetal, e.g., polyvinyl butyral, polyvinyl formal; polyformaldehydes.

- In the case where aqueous development of the
- 25 photosensitive composition is desirable, the branched polymer product and/or the binder should contain sufficient acidic or other groups to render the composition processible in aqueous developer. Useful aqueous-processible binders include those disclosed in
- 30 U.S. Patent 3,458,311 and in U.S. Patent 4,273,857. Useful amphoteric polymers include interpolymers derived from N-alkylacrylamides or methacrylamides, acidic film-forming comonomer and an alkyl or hydroxyalkyl acrylate

such as those disclosed in U.S. Patent 4,293,635. For aqueous development the photosensitive layer will be removed in portions which are not exposed to radiation but will be substantially unaffected during development
5 by a liquid such as wholly aqueous solutions containing 1% sodium carbonate by weight.

A particularly preferred class of polymeric binder modifiers are polyvinyl pyrrolidone polymers and copolymers and amphoteric polymers and copolymers.

10

PLASTICIZERS

The photopolymerizable compositions may also contain a plasticizer to modify adhesion, flexibility, hardness, solubility, and other mechanical or chemical
15 properties required during its processing or end use.

Suitable plasticizers include triethylene glycol, triethylene glycol diacetate, triethylene glycol dipropionate, triethylene glycol dicaprylate, triethylene glycol dimethyl ether, triethylene glycol
20 bis(2-ethylhexanoate), tetraethylene glycol diheptanoate, poly(ethylene glycol), poly(ethylene glycol) methyl ether, isopropyl naphthalene, diisopropyl naphthalene, poly(propylene glycol), glyceryl tributyrate, diethyl adipate, diethyl sebacate, dibutyl
25 suberate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, tris(2-ethylhexyl) phosphate, Brij® 30 [C₁₂H₂₅(OCH₂CH₂)₄OH], and Brij® 35 [C₁₂H₂₅(OCH₂CH₂)₂₀OH].

30 FILLERS

The photopolymerizable compositions may also contain particulates such as organic or inorganic fillers to modify the mechanical or chemical properties required

during its processing or end use. Suitable fillers include organic or inorganic reinforcing agents which are essentially transparent as disclosed in U.S. Patent 2,760,863, e.g., organophilic silica bentonite, silica, and powdered glass having a particle size less than 0.4 mil; inorganic thixotropic materials as disclosed in U.S. Patent 3,525,615 such as boehmite alumina, clay mixtures of highly thixotropic silicate oxide such as bentonite and finely divided thixotropic gel containing 99.5% silica with 0.5% mixed metallic oxide; microcrystalline thickeners as disclosed in U.S. Patent 3,754,920 such as microcrystalline cellulose and microcrystalline silicas, clays, alumina, bentonite, kalonites, attapulgites, and montmorillonites; finely divided powders having a particle size of 5 millimicrons to 50 microns as disclosed in U.S. Patent 3,891,441 such as silicon oxide, titanium oxide, carbon black, zinc oxide, and other commercially available pigments; and the binder-associated, transparent, inorganic particles as disclosed in European Patent Application 87113013.4 such as magnesium silicate (talc), aluminum silicate (clay), calcium carbonate and alumina. Typically, the filler will be transparent to actinic radiation to preclude adverse effects during imaging exposure. Depending on its function in the photopolymerizable composition, the filler may be colloidal or have an average particle size of 50 microns or more in diameter.

ADHESION PROMOTER

When the photopolymerizable composition is to be used as a coating on a metal surface, such as a photoresist, a heterocyclic or mercaptan compound may be added to improve adhesion of the coating to the metal required during processing or in the end-use product. Suitable adhesion promoters include heterocyclics such as those disclosed in Hurley et al. U.S. Patent 3,622,334, Jones U.S. Patent 3,645,772, and Weed U.S. Patent 4,710,262. Examples of useful adhesion promoters include benzotriazole, 5-chloro-benzotriazole, 1-chloro-benzotriazole, 1-carboxy-benzotriazole, 1-hydroxy-benzotriazole, 1,2-naphthotriazole, benzimidazole, mercaptobenzimidazole, 5-nitro-2-mercaptobenimidazole, 5-amino-2-mercaptobenzimidazole, 2-amino-benzimidazole, 5-methyl-benzimidazole, 4,5-diphenyl-benzimidazole, 2-guanadino-benzimidazole, benzothiazole, 2-amino-6-methyl-benzothiazole, 2-mercaptobenzothiazole, 2-methyl-benzothiazole, benzoxazole, 2-mercaptobenzoxazole, 2-mercaptothiazoline, benzotriazole, 3-amino-1,2,4-triazole, 1H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiodiazole-2-thiol, 4-mercapto-1H-pyrazolo[3,4-d]pyrimidine, 4-hydroxy-pyrazolo[3,4-d]pyrimidine, 5-amino-tetrazole monohydrate, tolutriazole, 1-phenyl-3-mercaptotetrazole, 2-amino-thiazole, and thio-benzanilide. Preferred adhesion promoters for use in photoresists and solder masks include benzotriazole, 5-chloro-benzotriazole, 1-chloro-benzotriazole, 1-carboxy-benzotriazole, 1-hydroxy-benzotriazole, 2-mercaptobenzoxazole, 1H-1,2,4-triazole-3-thiol, 5-amino-1,3,4-thiodiazole-2-thiol, and mercaptobenzimidazole.

OTHER COMPONENTS

The photopolymerizable compositions may contain other components such as thermal polymerization

- 5 inhibitors, dyes and pigments, optical brighteners and the like to stabilize, color or otherwise enhance the composition:

- Thermal polymerization inhibitors that can be used in the photopolymerizable compositions are: p-
10 methoxyphenol, hydroquinone, and alkyl and aryl-substituted hydroquinones and quinones, tert-butyl catechol, pyrogallol, copper resinate, naphthylamines, beta-naphthol, cuprous chloride, 2,6-di-tert-butyl-p-cresol, phenothiazine, pyridine, nitrobenzene and
15 dinitrobenzene, p-toluquinone and chloranil. Also useful for thermal polymerization inhibitors are the nitroso compositions disclosed in U.S. 4,168,982.

- Various dyes and pigments may be added to increase the visibility of the resist image. Any colorant used,
20 however, should preferably be transparent to the actinic radiation used.

- Useful optical brighteners include those disclosed in Held U.S. Patent 3,854,950. A preferred optical brightener is 7-(4'-chloro-6'-diethylamino-1',3',5'-
25 triazine-4'-yl) amino 3-phenyl coumarin. Ultraviolet radiation absorbing materials useful in the invention are also disclosed in Held U.S. Patent 3,854,950.

PHOTORESIST APPLICATIONS

- 30 The photopolymerizable compositions of this invention are particularly useful as photoresists for preparing printed circuit boards. In general the use of resists to prepare printed circuits is described in

"Printed Circuits Handbook", Second Edition, edited by C. F. Coombs, Jr, published by McGraw-Hill, Inc. in 1979 which includes both screen printed resists as well as photoresists. The use of conventional photoresists for preparing photocircuits is described in "Photoresist - Materials And Processes", by W. S. DeForest, published by McGraw-Hill, Inc. in 1975 which includes negative working photopolymerizable and photocrosslinkable or dimerizable systems as well as positive working photosolubilizable systems. Photoresists may be used in temporary coatings in a primary imaging process to make the printed circuit or they may be used in a secondary imaging process to make permanent coatings, e.g., a solder mask, to protect the circuit during subsequent processing or from environmental effects during use. Permanent coatings also are used as intermediate insulative layers in the manufacture of multilayer printed circuits.

In practice, a photopolymerizable layer, typically between 2.5 and 125 micrometers thick, is applied to a printed circuit substrate which typically is a copper clad fiberglass epoxy board for primary imaging or a printed circuit relief pattern on the board for secondary imaging. The applied photopolymerizable layer is then imagewise exposed to actinic radiation to harden or insolubilize exposed areas. The unexposed areas are then completely removed typically with a developer solution which selectively dissolves, strips or otherwise disperses the unexposed areas without adversely affecting the integrity or adhesion of the exposed areas. The surface areas of the substrate which were uncovered by the development process are then

modified by etching or removing material therefrom or depositing a material thereon.

In the instance of primary imaging to form a printed circuit board, the uncovered copper surface areas may be etched or removed to form a printed circuit directly, or additional copper or other metal resistant to etchant, e.g., gold, tin/lead, etc., may be plated thereover. In the first instance, the hardened exposed resist is typically removed from the remaining copper surface by a stripping process to form the circuit board directly. In the second instance, the hardened resist is first stripped from the unplated copper surface which is then etched or removed from the substrate to form a plated printed circuit board.

In the instance when a permanent resist or solder mask is formed on a printed circuit board, the developed solder mask resist image may first be treated to further cure or harden it by baking at elevated temperatures, by additional uniform exposure to actinic radiation or a combination thereof to produce a circuit board having a cured solder mask layer covering all areas except pad or through-hole areas. Electrical components are then inserted into the through-holes and soldered in place to form the packaged electrical component. In the instance when a multilayer printed circuit is to be prepared, a permanent resist may be applied to a catalyzed substrate, imaged, developed to uncover catalyzed areas then typically electrolessly plated to form a first circuit layer. The entire surface of the first circuit layer is then catalyzed and the process is repeated one or more times to form a multilayer printed circuit board.

A particularly preferred embodiment of this invention is a process for forming a solder mask on a printed circuit substrate bearing on its surface, a raised, conductive circuit pattern, the process

5 comprising the steps of

(1) applying to the substrate surface bearing the circuit pattern, a photopolymerizable composition to form a photopolymerizable layer thereon, the photopolymerizable composition comprising;

10

(A) a branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer, wherein

15

20

(a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,

25

(b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,

30

(c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and

- (d) the branch polymer segment(s) contain from about 35% to 100% of the hydrophilic groups; and
- (B) an addition polymerizable monomer containing at least one terminal, ethylenically unsaturated groups; and
- (C) an initiating system activated by actinic radiation;
- (2) imagewise exposing the layer to actinic radiation to form exposed and unexposed areas,
- (3) removing unexposed areas of the layer to form a stencil solder mask image in the exposed areas and complimentary, unprotected areas of the circuit pattern.
- In a specific embodiment of this process, (A) is a branched polymer product comprising a plurality of branch polymer segments chemically linked along a linear polymer backbone segment wherein the branch polymer segments are formed during addition polymerization of the branched polymer product from at least one ethylenically unsaturated macromer component containing one or more hydrophilic functional groups; wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 30,000 and a polydispersity (M_w/M_n) of not greater than about 5.

The photopolymerizable composition typically contains a thermally activated crosslinking component and after step (c) the resist areas typically are cured by heating, by uniformly exposing to actinic radiation, by treating with a chemical reagent or by a combination thereof.

Especially preferred for use in permanent coating compositions are branched polymer products in which the branched polymer product comprises a copolymer of BA/S/HEMA/Macromer (where the Macromer is a
5 BMA/MMA/HEMA/MAA copolymer, a BMA/HEMA/MAA copolymer or a BMA/MAA copolymer, each having a single terminal ethylenic group), with the respective monomer weight ratios in the branched polymer product being about 48/15/15/22, the respective ratios in the macromer being
10 about 43/2/30/25, 45/30/25 or 75/25. In the designated branched polymer product BA is butyl acrylate; BMA is butyl methacrylate; HEMA is 2-hydroxyethyl methacrylate; MAA is methacrylic acid; MMA is methyl methacrylate; and S is styrene.

15

RESIST APPLICATION

The photopolymerizable resists may be applied to a printed circuit substrate either as a liquid, as a pre-formed dry film, or as a combination of a liquid and dry
20 film.

COATING LIQUIDS

The photopolymerizable resist may be coated as a liquid onto the printed circuit substrate using any
25 conventional coating process. The liquid may be a solution of the resist wherein the solvent is removed subsequent to coating to form a dry, solid, resist layer, or the liquid may be a neat, solvent-free, resist which, subsequent to coating, is directly imaged or
30 exposed to actinic radiation to form a hardened resist layer. The liquids may be roller-coated, spin-coated, screen-coated or -printed as disclosed in Coombs supra, in DeForest supra, in Lipson et al. U.S. Patent

4,064,287, or in Oddi et al. U.S. Patent 4,376,815. The liquid, typically as a solution, may also be curtain coated as disclosed in Losert et al. U.S. Patent 4,230,793. Neat liquids may be coated and imaged using processes as disclosed in Heiart U.S. Patent 4,548,884, Hauser U.S. Patent B1 4,528,261 or Sullivan U.S. Patents 4,424,089 and 4,591,265.

DRY FILM LAMINATION

10 A pre-formed, dry-film, photopolymerizable resist layer typically is applied from a multi-ply, transfer, resist element using the lamination process as described in Celeste U.S. Patent 3,469,982. The multi-ply, resist element comprises, in order, an actinic-radiation
15 transparent, temporary support film, e.g., polyethylene terephthalate, a thin photopolymerizable resist layer, and optionally a removable cover sheet, e.g., polyethylene, to protect the resist element during storage. As described in Celeste supra, the cover
20 sheet, if present, is first removed and the uncovered photoresist surface is laminated to the surface of a copperclad printed circuit substrate using heat and/or pressure, e.g., with a conventional hot-roll laminator. Although the laminate is typically imagewise exposed to
25 actinic radiation through the temporary support film, in some instances, where the photoresist layer is insensitive to ambient constituents, like oxygen, the temporary support may be removed before imaging to improve resolution and other such properties. In some
30 instances resist adhesion to the substrate can be improved by treating the substrate surface with a liquid at or just prior to lamination. Typically, the liquid is insensitive to actinic radiation and may be a

solution of adhesion promoters as disclosed in Jones U.S. Patent 3,645,772, a solvent or swelling agent for the resist layer as disclosed in Fickes U.S. Patent 4,069,076, a non-solvent, as disclosed in Cohen U.S. Patent 4,405,394 and European Patent 0041639, Pilette et al. U.S. Patent 4,378,264, and Weiner et al. European Patent 0040842, or a liquid component of the resist layer as disclosed in Lau et al. U.S. Patent 4,698,294. The liquid in some instances may be photosensitive such as the photoresist solutions disclosed in Isaacson U.S. Patent 3,629,036, photosensitive liquids as disclosed in O'Neil et al., European Patent Application 87113176.9, or neat photoresist liquids as disclosed in Sullivan U.S. Patent 4,506,004.

In instances when a dry film, e.g., solder mask, is to be laminated to a substrate having a low relief like a circuit board, measures must be taken to eliminate entrapped air, e.g., from around circuit lines. Entrapped air is eliminated by the vacuum lamination process of Friel U.S. Patent 4,127,436, by the grooved roll lamination process of Collier et al. U.S. Patent 4,071,367, or by using liquid treating agents as described in Fickes supra, Lau et al. supra, O'Neil et al. supra or Sullivan '004 supra.

To further illustrate the present invention the following examples are provided, wherein the amounts of components are given in parts by weight unless otherwise designated.

30

Example 1

Macromer Solution (1) to be used in subsequent branched polymer product formation, is prepared using the following procedures:

To a clean reaction vessel were added:

	<u>Amount</u>	
	Methacrylic acid (MAA)	3.31
5	Hydroxyethyl methacrylate (HEMA)	7.93
	Butyl methacrylate (BMA)	11.89
	Methyl ethyl ketone	15.50

The resulting solution was heated to reflux
10 temperature and held there, with stirring. The
following solution, previously mixed for 15 minutes
under nitrogen was then rapidly added:

		<u>Amount</u>
15	Methyl ethyl ketone	1.56
	Bis(difluoroboryl) diphenyl gloximato cobalt II hydrate (SCT)	0.004
	Vazo®52 catalyst	0.023
20	2,2'-azobis(2,4- dimethylpentane nitrile)	

The following solutions, previously mixed for 15
minutes under nitrogen, were then simultaneously added
25 to the reaction vessel:

	<u>Solution (A)</u>	<u>Amount</u>
	Methyl ethyl ketone	8.79
	SCT	0.007
30	Vazo®52	0.252

	<u>Solution (B)</u>	<u>Amount</u>
	Methacrylic acid (MAA)	7.68
	Hydroxyethyl methacrylate (HEMA)	5.29
	Butyl methacrylate (BMA)	7.93
5	Methyl ethyl ketone	0.55

Solution (A) was fed so that 54.8% was added over a 90-minute period and the remaining 45.2% was added over an additional 240-minute period; solution (B) was fed so
10 that 67% was added over a 120-minute period and the remaining 33% was added over an additional 120-minute period.

The reaction mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.9 parts of
15 methyl ethyl ketone were added. The mass was then held for another 30 minutes at reflux temperature, cooled to 50°C and filtered to give Macromer Solution (1).
Molecular weights were measured using conventional gel permeation chromatography (GPC) methods. The weight
20 average molecular weight (M_w) was 4618 and the number average molecular weight was 2152 to give a polydispersity (M_w/M_n) of 2.15.

Branched Polymer Product (A) was prepared using the following procedures:

25 To a reaction vessel were added:

	<u>Amount</u>	
	Macromer Solution (1)	16.00
	Butyl acrylate (BA)	20.94
30	Styrene (S)	6.54
	Hydroxyethyl methacrylate (HEMA)	6.54
	Methyl ethyl ketone	10.83

This reaction mass was heated to reflux temperature and held there, with stirring, while there was added, over a 5-minute period, a solution of:

5		<u>Amount</u>
	Methyl ethyl ketone	2.18
	Vazo®67 (2,2'-azobis(2-methylpentane nitrile)	0.96

- 10 This was flushed with additional methyl ethyl ketone (1.03), and the reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

The following solution was then added to the reaction mass:

15		<u>Amount</u>
	Methyl ethyl ketone	1.31
	Vazo®67	0.57

- 20 This was flushed with additional methyl ethyl ketone (0.33), and, the reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

The following solution was then added:

25		<u>Amount</u>
	Methyl ethyl ketone	0.87
	Vazo®67	0.22

- 30 This was flushed with additional methyl ethyl ketone (0.13), and the reaction mass was then held at reflux temperature, with stirring, for 120 minutes to give a polymer product, Branched Polymer Product (A), which is:

BA/S/HEMA/Macromer
48/15/15/22

where Macromer is:

5 BMA/HEMA/MAA
 45/30/25

For simplicity, a linear polymer without arms (not
of this invention) was subsequently polymerized in this
10 solution, as described below.

To the solution above, the following solution was
added:

	<u>Amount</u>
15 Methacrylic acid	0.58
Methyl methacrylate	4.27
Methyl ethyl ketone	7.06

followed by a solution containing:

	<u>Amount</u>
20 Methyl ethyl ketone	0.34
Vazo®R67	0.13

25 This was flushed with additional methyl ethyl ketone
(0.24). The reaction mass was again held at reflux
temperature for 120 minutes, with stirring, and then the
following solution was added:

	<u>Amount</u>
30 Methyl ethyl ketone	0.145
Vazo®34	0.068

This was flushed with additional methyl ethyl ketone (0.04). The mass was then held at reflux temperature, with stirring, for 240 minutes, to give a polymer product, Polymer Product (B), which is:

5

MMA/MAA
88/12

This mixture was formed into pellets by drying it in an extrusion devolatilizer, having a weight average molecular weight (M_w) of 24,658. Glass transition temperatures, measured by differential scanning calorimetry, were -11.1°C and 28.4°C .

15

Example 2

A dry-film, photosensitive solder mask element was prepared as follows:

<u>Solder Mask Composition</u>	<u>Amount</u>
Pentaerythritol triacrylate	450.0
Trimethylol propane triacrylate	450.0
Homopolymer of hexamethylene diisocyanate blocked with methyl ethyl ketoxime	817.8
(75% solids)	
Diethyl hydroxylamine	1.5
Benzophenone	120.0
Michler's ketone	3.0
3-mercapto-1H-1,2,4-triazole	6.0
Green colorant (Dayglo® 122-9655)	90.0
Mixture of Branched Polymer Product (A) and Polymer Product (B) of Example 1	1264.5
Amphoteric copolymer formed from	60.0

40% N-t-octyl acrylamide, 34% methyl
methacrylate, 16% acrylic acid,
6% hydroxypropyl methacrylate and
4% t-butyl aminoethyl methacrylate;
5 mol. wt. ca. 50,000
PVP K-90 (polyvinyl Pyrrolidone) 180.0

The composition was dissolved for coating in 5365
parts by weight of solvent comprising 90% methylene
10 chloride and 10% methanol. This solution was then
coated on Mylar®92D polyethylene terephthalate film
(E. I. du Pont de Nemours and Company) and air-dried at
150°F to give a dry photosensitive layer 2 mils thick.
This layer was top-laminated with matte, 1 mil
15 polyethylene film with the smooth side to the coating,
to give a dry-film, photosensitive, solder mask element.

A series of printed circuit board panels of a size
12"x18" containing a raised relief height of about 3.5
mils on both panel surfaces with approximately 1200
20 holes ranging in size from 17 mils to 35 mils diameter
was coated with tripropyleneglycol diacrylate (having a
viscosity of 14.5 centipoise at 25°C) via a wetting
sponge.

The monomer wet panels while held in a vertical
25 position were passed in a horizontal direction through a
nip of two rolls while the dry photosensitive layer was
laminated onto the wet panels after first removing the
polyethylene film therefrom. The temperature of the
rolls was about 140°F with nip pressure of about 35 psi
30 controlled by air cylinders. Each roll was of a type
employed in a VALU™ System lamination but contained a
Teflon® polytetrafluoroethylene sleeve covering a normal
rubber coating.

In the lamination procedure the monomer of liquid coating was present in a thickness of about 0.2 mils measured away from the raised relief of the panel with the coating ranging to about 3.5 mils immediately adjacent the raised relief and approximately 0.2 mils above the raised relief.

The panel edges were trimmed and residual monomer liquid was removed by a spray of water.

The panels were held for 30 minutes after lamination and then given an exposure of 300 millijoules/cm² to ultraviolet light on Du Pont's PC-130 exposure unit. After exposure the Mylar® polyethylene terephthalate film was removed and the sample was developed in an ADS processor with a 1% aqueous sodium carbonate solution at 105°F. Development time was about 180 seconds. After development, each side of each board was cured in an Argus UV unit, first for an exposure of 2 joules/cm², then cooling the board, then for an exposure of 6 joules/cm². The boards were then baked for one hour at 150°C. The resulting solder mask permanently adhered to each printed circuit board.

The boards gave successful results as a solder mask when evaluated in a typical manner for solder mask properties including tests for solder resistance, solvent resistance, electrical properties, adhesion, thermal shock resistance and flammability. Testing followed the standard specification procedure recommended by the Institute for Interconnecting and Packaging Electronic Circuits present in their publication IPC-SM-840.

Example 3

Macromer Solution (2) to be used in subsequent branched polymer product formation, was prepared using the following procedures:

5

To a clean reaction vessel were added:

STEP I

		<u>Amount</u>
10	Methacrylic acid (MAA)	3.21
	Hydoxyethyl methacrylate (HEMA)	7.70
	Butyl methacrylate (BMA)	11.04
	Methyl methacrylate (MMA)	0.51
	Acetone	15.05

15

The resulting solution was heated to reflux temperature and held there, with stirring. The following solution, previously mixed for 15 minutes under nitrogen was then rapidly added:

20

STEP II

		<u>Amount</u>
	Acetone	3.04
	Bis(difluoroboryl) diphenyl	0.0008
25	gloximato cobalt II	
	hydrate (SCT)	
	Vazo®52 catalyst	0.0084
	[2,2'-azobis(2,4-	
	dimethylpentane nitrile)]	

30

The following solutions, previously mixed for 15 minutes under nitrogen, were then simultaneously added:

STEP III

	Solution (A)	Amount
	Acetone	8.53
	SCT	0.0014
5	Vazo®52	0.0918

STEP IV

	Solution (B)	Amount
	Methacrylic acid (MAA)	7.46
10	Hydroxyethyl methacrylate (HEMA)	5.14
	Butyl methacrylate (BMA)	7.36
	Methyl Methacrylate (MMA)	0.34
	Acetone	0.53

- 15 Solution (A) was fed so that 54.8% was added over a 90-minute period and the remaining 45.2% was added over an additional 240-minute period; Solution (B) was fed so that 67% was added over a 120-minute period and the remaining 33% was added over an additional 120-minute
- 20 period. After addition is over, Solutions (A) and (B) containers are flushed with 0.35 and 0.53 parts of acetone respectively and added into the reaction vessel. The reaction mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.71 parts of acetone
- 25 were added. The mass was then held for another 30 minutes at reflux temperature, cooled to 50°C and filtered to give Macromer Solution (2). Molecular weights were measured using conventional gel permeation chromatography (GPC) methods. The weight average
- 30 molecular weight (M_w) was 7562 and the number average molecular weight was 4409 to give a polydispersity (M_w/M_n) of 1.72. The calculated acid number of the macromer in Macromer Solution (2) is 162. Branched

Polymer Product (B) was prepared using the following procedures:

To a reaction vessel were added:

5	<u>STEP V</u>	
		<u>Amount</u>
	Macromer Solution (2)	22.34
	Butyl acrylate (BA)	15.94
	Hydroxyethyl methacrylate (HEMA)	6.26
10	Methyl methacrylate (MMA)	6.26
	Styrene (S)	0.102
	Methacrylic acid (MAA)	0.102
	acetone	1.81

- 15 This reaction mass was heated to reflux temperature and held there, with stirring, while there was added, over a 5-minute period, a solution of:

	<u>STEP VI</u>	
20		<u>Amount</u>
	Acetone	1.05
	Vazo®52	0.1253

- 25 This was flushed with additional acetone (1.0), and the reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

The following solution was then added to the reaction mass:

30	<u>STEP VII</u>	
		<u>Amount</u>
	Acetone	0.42
	Vazo®52	0.0205

This was flushed with additional acetone (0.4), and, the reaction mass was then held at reflux temperature, with stirring, for 120 minutes.

- 5 The following solution was then added to the reaction mass:

STEP VIII

		<u>Amount</u>
10	Acetone	0.42
	Vazo® 67 (2,2'-azobis(2-methylpentane nitrile)	0.0102

- 15 This was flushed with additional acetone (0.4), and the reaction mass was then held at reflux temperature, with stirring, for 180 minutes. The polymer solution was then diluted with acetone (11.79, STEP IX), cooled to 50°C and filtered to give a polymer product, Branched Polymer Product (B), which is:

- 20 BA/HEMA/MMA/S/MAA/Macromer
 38 .92/15.29/15.29/0.25/0.25/30

where Macromer is:

BMA/HEMA/MMA/MAA
 43/30/2/25

- 25 The molecular weight of Branched Polymer Product (B) was measured using gel permeation chromatography. The weight average molecular weight (M_w) was 140,386 and the number average molecular weight (M_n) was 28,728 to give a polydispersity (M_w/M_n) of 4.89. The weight ratio
- 30 of the backbone segment to branch polymer segments of Branched Polymer Product (B) is 70/30. The calculated acid number for Branched Polymer Product (B) is 49. The branch polymer segments contain 60.5% by weight of the

hydrophilic groups present in the Branched Polymer Product (B).

Example 4

5 A dry-film, photosensitive solder mask element was prepared and processed as described in Example 2 except that the solder mask formulation was as follows:

	<u>Solder Mask Composition</u>	<u>Amount</u>
	Pentaerythritol triacrylate	6,768
	Trimethylol propane triacrylate	6,768
10	Homopolymer of hexamethylene diisocyanate blocked with methyl ethyl ketoxime (75% solids)	4,500
	Diethyl hydroxylamine	18
	Benzophenone	1,260
15	Ethyl Michler's ketone	108
	3-mercapto-1H-1,2,4-triazole	72
	Colorant (Penncolor 9G5)	360
	Green colorant (Dayglo 122-9655)	540
	Branched Polymer Product (B)	23,836
20	of Example 3 (60% solids)	
	Treated talc (Cyprubond®) dispersed in solution of branded polymer product (B) of Example 3	5,400
	Amphoteric copolymer formed from	990
25	40% N-t-octyl acrylamide, 34% methyl methacrylate, 16% acrylic acid, 6% hydroxypropyl methacrylate and 4% t-butyl aminoethyl methacrylate; mol. wt. ca. 50,000	
30	PVP K-90 (polyvinyl Pyrrolidone)	1,440

The composition was dissolved in 16,341 parts by weight of additional acetone and 27,000 parts by weight

of methanol. This solution was coated and evaluated in the manner similar to that described in Example 2.

The boards gave successful results as a solder mask when evaluated in a typical manner for solder mask properties including tests for solder resistance, solvent resistance, electrical properties, adhesion, thermal shock resistance and flameability. Testing followed the standard specification procedure recommended by the Institute for Interconnecting and Packaging Electronic Circuits present in their publication IPC-SM-840.

Example 5

Macromer Solutions (3) and (4) to be used in subsequent branched polymer product formation, is prepared using the procedures of Example 3:

To a clean reaction vessel were added:

STEP I

	<u>Macromer</u>	(3)	(4)
		<u>Amount</u>	<u>Amount</u>
	Methacrylic acid (MAA)	3.21	3.21
	Hydoxyethyl methacrylate (HEMA)	7.69	7.69
	Butyl methacrylate (BMA)	11.02	11.02
25	Methyl methacrylate (MMA)	0.51	0.51
	Acetone	15.03	-
	Methyl ethyl ketone (MEK)	-	15.03

Each resulting solution was heated to reflux temperature and held there, with stirring. The following solution, previously mixed for 15 minutes under nitrogen was then rapidly added:

56

STEP II

	<u>Macromer</u>	(3) <u>Amount</u>	(4) <u>Amount</u>
	Acetone	3.03	-
5	MEK	-	2.96
	SCT	0.0008	0.0034
	Vazo® 52 catalyst	0.1105	0.0224

The following solutions, previously mixed for 15
 10 minutes under nitrogen, were then simultaneously added:

STEP III

	<u>Macromer</u>	(3) <u>Amount</u>	(4) <u>Amount</u>
	Solution (A)		
15	Acetone	8.52	-
	MEK	-	8.52
	SCT	0.0014	0.0064
	Vazo®52	0.0917	0.2445

20

STEP IV

	<u>Macromer</u>	(3) <u>Amount</u>	(4) <u>Amount</u>
	Solution (B)		
	Methacrylic acid (MAA)	7.45	7.45
	Hydroxyethyl methacrylate (HEMA)	5.13	5.13
25	Butyl methacrylate (BMA)	7.35	7.35
	Methyl Methacrylate (MMA)	0.34	0.34
	Acetone	0.53	-
	MEK	-	0.53

30 For Macromer (3) - Solution (A) was fed so that 67% was
 added over a 60-minute period and the remaining 33% was
 added over an additional 120-minute period. Solution
 (B) was fed so that 67% was added over a 60-minute

period and the remaining 33% was added over an additional 120-minute period.

For Macromer (4) - Solution (A) was fed so that 54.8% was added over a 90-minute period and the
5 remaining 45.2% was added over an additional 240-minute period. Solution (B) was fed so that 67% was added over a 120-minute period and the remaining 33% was added over an additional 120-minute period.

After the additions are complete, Solutions (A) and
10 (B) containers are flushed with 0.35 and 0.53 parts of solvent (acetone for Macromer (3) and MEK for Macromer (4)) respectively and added into the reaction vessels. Each reaction mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.71 parts of solvent
15 were added. Each reaction mass was then held for another 30 minutes at reflux temperature, cooled to 50°C and filtered to give Macromer Solutions (3) and (4). Molecular weights were measured using conventional gel permeation chromatography (GPC) methods.

20 For Macromer (3) - The weight average molecular weight (M_w) was 28,165 and the number average molecular weight (M_n) was 8,415 to give a polydispersity (M_w/M_n) of 3.34.

For Macromer (4) - The weight average molecular
25 weight (M_w) was 4,570 and the number average molecular weight (M_n) was 3,030 to give a polydispersity (M_w/M_n) of 1.51.

Branched Polymer Products (C) and (D) were prepared using the following procedures:

30 To each reaction vessel were added:

STEP V

<u>Branch Polymer Product</u>		(C)	(D)
		<u>Amount</u>	<u>Amount</u>
	Macromer Solution (3)	22.34	-
5	Macromer Solution (4)	-	22.36
	Butyl acrylate (BA)	15.94	15.96
	Hydroxyethyl methacrylate (HEMA)	6.26	6.27
	Methyl methacrylate (MMA)	6.26	6.27
	Styrene (S)	0.102	0.102
10	Methacrylic acid (MAA)	0.102	0.102
	Acetone	1.81	-

Each reaction mass was heated to reflux temperature and held there, with stirring, while there was added, over a
15 5-minute period, a solution of:

STEP VI

<u>Branch Polymer Product</u>		(C)	(D)
		<u>Amount</u>	<u>Amount</u>
	Acetone	1.05	-
20	MEK	-	1.05
	Vazo®52	0.1253	0.0627

Product (C) reaction mass was flushed with additional acetone (1.0), and the reaction mass was then held at
25 reflux temperature, with stirring, for 120 minutes.
Product (D) reaction mass was flushed with additional MEK (1.0), and the reaction mass was then held at 80 to 84°C, with stirring, for 180 minutes.

The following solutions were then added to each
30 respective reaction mass:

STEP VII

<u>Branch Polymer Product</u>		(C)	(D)
		<u>Amount</u>	<u>Amount</u>
5	Acetone	0.42	-
	MEK	-	0.42
	Vazo®52	0.0205	0.0102

Product (C) reaction mass was flushed with additional acetone (0.4), and the reaction mass was then held at reflux temperature, with stirring, for 120 minutes. Product (D) reaction mass was flushed with additional MEK (0.4), and the reaction mass was then held at 80 to 84°C, with stirring, for 180 minutes.

The following solutions were then added to each respective reaction mass:

STEP VIII

<u>Branch Polymer Product</u>		(C)	(D)
		<u>Amount</u>	<u>Amount</u>
20	Acetone	0.42	-
	MEK	-	0.42
	Vazo®67 (2,2'-azobis(2-methylpentane nitrile)	0.0102	0.0102

Product (C) reaction mass was flushed with additional acetone (0.4), and the reaction mass was then held at reflux temperature, with stirring, for 180 minutes. The polymer solution was then diluted with 11.79 parts by weight acetone, cooled to 50°C and filtered to give Branched Polymer Product (C). Product (D) reaction mass was flushed with additional MEK (0.4), and the reaction mass was then held at 80 to 84°C with stirring, for 180 minutes. The polymer solution was then diluted with

13.62 parts by weight MEK, cooled to 50°C and filtered to give Branched Polymer Product (B).

Each Branch Polymer Product had the same composition which is:

5 BA/HEMA/MMA/S/MAA/Macromer
 38 .92/15.29/15.29/0.25/0.25/30

where Macromer is:

 BMA/HEMA/MMA/MAA
 43/30/2/25

10 The molecular weight of Branched Polymer Products were measured using gel permeation chromatography.

 For Branch Polymer Product (C), the weight average molecular weight (M_w) was 399,000 and the number average molecular weight (M_n) was 44,700 to give a
15 polydispersity (M_w/M_n) of 8.93.

 For Branch Polymer Product (D), the weight average molecular weight (M_w) was 34,500 and the number average molecular weight (M_n) was 9,200 to give a polydispersity (M_w/M_n) of 3.75.

20 Each of the Branch Polymer Products (C) and (D) may be used as the polymeric binder component in alkaline, aqueous processable photoresist and photosensitive solder mask formulations for the manufacture of printed circuit boards and the like.

25

Example 6

 Macromer Solution (5) to be used in preparing a branched polymer product with amino functionality, was prepared using the following procedures:

30

 To a clean reaction vessel were added:

61

STEP I

	<u>Amount</u>
Dimethylaminoethyl methacrylate (DMAEMA)	4.71
5 Methyl methacrylate (MMA)	17.73
MEK	15.03

The resulting solution was heated to reflux temperature and held there, with stirring. The following solution, previously mixed for 15 minutes under nitrogen was then rapidly added:

STEP II

	<u>Amount</u>
15 MEK	2.95
SCT	0.0013
Vazo®52	0.0224

The following solutions, previously mixed for 15 minutes under nitrogen, were then simultaneously added:

STEP III

	<u>Amount</u>
Solution (A)	
MEK	8.52
25 SCT	0.0021
Vazo®52	0.2445

STEP IV

	<u>Amount</u>
Solution (B)	
30 DMAEMA	4.26
MMA	16.01
MEK	0.53

Solution (A) was fed so that 54.8% was added over a 90-minute period and the remaining 45.2% was added over an additional 240-minute period. Solution (B) was fed so that 67% was added over a 120-minute period and the remaining 33% was added over an additional 120-minute period. After addition is over, Solutions (A) and (B) containers are flushed with 0.35 and 0.53 parts of MEK respectively and added into the reaction vessel. The reaction mass was held at reflux temperature, with stirring, for 45 minutes, and then 6.71 parts of MEK were added. The mass was then held for another 30 minutes at reflux temperature, cooled to 50°C and filtered to give Macromer (5) which is:

MMA/DMAEMA

15

79/21

Molecular weights were measured using conventional gel permeation chromatography (GPC) methods. The weight average molecular weight (M_w) was 7,778 and the number average molecular weight was 3,089 to give a polydispersity (M_w/M_n) of 2.51. The calculated amine number of Macromer (5) is 42.

Macromer (5) containing amino groups may be used to prepare a branch polymer products that could be used as the polymeric binder component in acid, aqueous processable photoresist formulations for the manufacture of printed circuit boards and the like. Such formulations may be processed with aqueous solutions containing lactic, acetic, formic, or phosphoric acid or the like.

What is claimed is:

1. A branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer, wherein
 - (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,
 - (b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,
 - (c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and
 - (d) the branch polymer segment(s) contain from about 35% to 100% of the hydrophilic groups.
2. The branched polymer product of claim 1 wherein the hydrophilic group is a protic group.
3. The branched polymer product of claim 1 wherein the hydrophilic group is hydroxy, amino, ammonium, amido, imido, urethano, ureido, or mercapto; or carboxylic, sulfonic, sulfinic, phosphoric, or phosphonic acids or salts thereof.
4. The branched polymer product of claim 1 wherein the hydrophilic groups are acid groups, the ethylenically unsaturated macromer component has an acid number between about 50 and about 650, and the branch

polymer product has an acid number between about 20 and about 90.

5. The branched polymer product of claim 1 wherein the hydrophilic groups are amine groups, wherein the
5 ethylenically unsaturated macromer component has an amine number between about 35 and about 650, and the branch polymer product has an amine number between about 20 and about 90.

6. The branched polymer product of claim 1 wherein
10 the macromer component has a weight average molecular weight (M_w) of several hundred to about 40,000.

7. The branched polymer product of claim 6 wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of about 6,000 to
15 about 15,000.

8. The branched polymer product of claim 1 wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) equivalent to the molecular weight of 2 to about 500 monomer units used to
20 form the macromer component.

9. The branched polymer product of claim 8 wherein the ethylenically unsaturated macromer component contains between 30 and 200 monomeric units.

10. The branched polymer product of claim 1 wherein
25 the ethylenically unsaturated macromer component comprises at least 0.5 weight % of the components used to form the branched polymer product.

11. The branched polymer product of claim 10 wherein the ethylenically unsaturated macromer component
30 comprises between about 0.5 and about 80 weight % of the components used to form the branched polymer product.

12. The branched polymer product of claim 1 wherein the ethylenically unsaturated macromer component is a

linear polymer, copolymer or oligomer containing a terminal ethylenic group and wherein the macromer component is formed by free radical polymerization of one or more vinyl monomers.

5 13. The branched polymer product of claim 12 wherein the macromer component is formed from at least one or more vinyl monomers selected from the group consisting of acrylic, methacrylic, itaconic or maleic acids and their anhydrides, esters, amides, imides or
10 nitriles.

14. The branched polymer product of claim 12 wherein vinyl monomer is selected from the group consisting of methyl methacrylate (MMA); ethyl methacrylate (EMA); butyl methacrylate (BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl
15 acrylate (EA); butyl acrylate (BA); 2-ethylhexyl acrylate; 2-hydroxyethyl methacrylate (HEMA); 2-hydroxyethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); itaconic acid (IA) and itaconic acid anhydride, half ester and imide; maleic acid and maleic
20 acid anhydride, half ester and imide; aminoethyl methacrylate; t-butyl aminoethyl methacrylate; dimethyl aminoethyl methacrylate; diethyl aminoethyl methacrylate; aminoethyl acrylate; dimethyl aminoethyl
25 acrylate; diethyl aminoethyl acrylate; acrylamide; N-t-octyl acrylamide; vinyl methyl ether; styrene (S); alpha-methyl styrene; vinyl acetate; and vinyl chloride.
15. The branched polymer product of claim 1 wherein the ethylenically unsaturated comonomer component is a free
30 radical polymerizable vinyl monomer.

16. The branched polymer product of claim 15 wherein the vinyl monomer is selected from the group consisting of acrylic, methacrylic, itaconic or maleic

acids and their anhydrides, esters, amides, imides or nitriles.

17. The branched polymer product of claim 15 wherein the vinyl monomer is selected from the group consisting of methyl methacrylate (MMA); ethyl methacrylate (EMA); butyl methacrylate (BMA); 2-ethylhexyl methacrylate; methyl acrylate (MA); ethyl acrylate (EA); butyl acrylate (BA); 2-ethylhexyl acrylate; 2-hydroxyethyl methacrylate (HEMA); 2-hydroxyethyl acrylate (HEA); methacrylic acid (MAA); acrylic acid (AA); itaconic acid (IA) and itaconic acid anhydride, half ester and imide; maleic acid and maleic acid anhydride, half ester and imide; aminoethyl methacrylate; t-butyl aminoethyl methacrylate; dimethyl aminoethyl methacrylate; diethyl aminoethyl methacrylate; aminoethyl acrylate; dimethyl aminoethyl acrylate; diethyl aminoethyl acrylate; acrylamide; N-t-octyl acrylamide; vinyl methyl ether; styrene (S); alpha-methyl styrene; vinyl acetate; and vinyl chloride.
18. The branched polymer product of claim 1 wherein at least one of the branch polymer segments, the linear polymer backbone segment, the ethylenically unsaturated macromer component or the ethylenically unsaturated comonomer component bears one or more functional groups wherein the functional group is -COOR; -OR; -SR (where R can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl, a heterocyclic, or -OR₁ where R₁ can be alkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); -CN; halogen; -NR₂R₃ or $\overset{\text{O}}{\parallel}\text{-C-NR}_2\text{R}_3$ (where R₂ and R₃ can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl, aralkyl, -CH₂OR₄ (where R₄ is hydrogen, alkyl or cycloalkyl of 1-12

carbon atoms, aryl, alkaryl, aralkyl), or together R₂ and R₃ can form a heterocyclic ring); $-\overset{\text{R}_5}{\underset{|}{\text{C}}}=\text{CR}_6\text{R}_7$ (where R₅, R₆ and R₇ can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl, aralkyl, or -COOR or when taken together R₅, R₆ and/or R₇ can form a cyclic group); -SO₃H; a urethane group; an isocyanate or blocked isocyanate group; a urea group; an oxirane group; an aziridine group; a quinone diazide group; an azo group; an azide group; a diazonium group; an acetylacetoxy group; -SiR₈R₉R₁₀ (where R₈, R₉ and R₁₀ can be alkyl or cycloalkyl of 1-12 carbon atoms or -OR₁₁ where R₁₁ is alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); or an -OSO₃R₁₂, -OPO₂R₁₂, -PO₂R₁₂, -PR₁₂R₁₃R₁₄, -OPOR₁₂, -SR₁₂R₁₃, or -N⁺R₁₂R₁₃R₁₄ group (where R₁₂, R₁₃ and R₁₄ can be hydrogen, alkyl or cycloalkyl of 1-12 carbon atoms, aryl, alkaryl or aralkyl); or a salt or onium salt of any of the foregoing.

19. The branched polymer product of claim 18 wherein the functional group is a carboxy, a hydroxy, an amino group, an amide group, a vinyl group, a urethane group, an isocyanate group, a blocked isocyanate group or combinations thereof.

20. The branched polymer product of claim 18 wherein at least one of the branched polymer segments or ethylenically unsaturated macromer components bears one or more carboxy, hydroxy, amino, an amide group, a vinyl group, a urethane group, an isocyanate group, a blocked isocyanate group or combinations thereof.

21. The branched polymer product of claim 1 wherein the macromer component is formed by a free radical

polymerization process employing a cobalt compound as a catalytic chain transfer agent.

22. The branched polymer product of claim 21 wherein the cobalt compound is a cobalt(II) compound.

5 23. The branched polymer product of claim 22 wherein the cobalt(II) compound is a pentacyanocobalt(II) compound or a cobalt(II) chelate of a vicinal iminohydroxyimino compound, a dihydroxyimino compound, a diazadihydroxyimninodialkyldecadiene, a
10 diazadihydroxyimninodialkylundecadiene, a tetraaza-tetraalkylcyclotetradecatetraene, a tetraaza-tetraalkylcyclododecatetraene, a bis(difluoroboryl) diphenyl glyoximato, a bis(difluoroboryl) dimethyl glyoximato, a N,N'-bis(salicylidene)ethylenediamine, a
15 dialkyldiazadioxodialkyldecadiene, or a dialkyldiazadioxodialkyltridecadiene.

24. A sensitive composition comprising

- (A) a branched polymer product containing hydrophilic groups comprising one or more
20 branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated
25 macromer component and at least one ethylenically unsaturated comonomer, wherein
- (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater
30 than 40,000,
- (b) the linear polymer backbone segment has a weight average molecular weight

(M_w) between about 10,000 and about 500,000,

(c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and

(d) the branch polymer segment(s) contain from about 35% to 100% of the hydrophilic groups, and

(B) at least one photoactive or thermally active component.

25. The sensitive composition of claim 24 in which component (B) cyclizes, dimerizes, polymerizes, crosslinks, generates a free radical, generates an ionic species or dissociates on exposure to actinic radiation.

26. The sensitive composition of claim 24 in which component (B) is a photoinitiator, a photosensitizer or a combination thereof.

27. The sensitive composition of claim 24 in which component (B) is a photosolubilizer.

28. The sensitive composition of claim 24 in which component (B) is a photodesensitizer.

29. The sensitive composition of claim 24 in which component (B) is a photoinhibitor.

30. The sensitive composition of claim 24 in which component (B) is a photodegradable component.

31. The sensitive composition of claim 24 in which component (B) is photochromic.

32. The sensitive composition of claim 24 in which component (B) is photoreducible or photo-oxidizable.

33. The sensitive composition of claim 24 in which component (B) is photoadhesive or photoreleaseable.

34. The sensitive composition of claim 24 in which component (B) is a phototackifier or a photodetackifier.

35. The sensitive composition of claim 24 in which component (B) is a material which changes or causes
5 changes in refractive index upon exposure to actinic radiation.

36. The sensitive composition of claim 24 in which component (B) is photomagnetic or a photodemagnetic.

37. The sensitive composition of claim 24 in which
10 component (B) is photoconductive or photoinsulative.

38. The sensitive composition of claim 24 in which component (B) is bonded to component (a).

39. The sensitive composition of claim 24 in which component (B) comprises:

- 15 (i) a polymerizable monomer, and
 (ii) an initiating system activatable by actinic radiation.

40. The sensitive composition of claim 39 in which the polymerizable monomer contains one or more
20 ethylenically unsaturated groups.

41. The sensitive composition of claim 39 in which the polymerizable monomer is at least one vinyl or acrylic compound or combinations thereof.

42. The sensitive composition of claim 24 further
25 comprising a linear, branched or network polymer, an inorganic particulate material or combinations thereof.

43. The sensitive composition of claim 24 having dispersed therein a colorant.

44. The sensitive composition of claim 24 further
30 comprising at least one thermally activated curing agent.

45. A process for imaging a photosensitive layer on a substrate comprising the steps of

(1) applying to a substrate, a photosensitive composition to form the photosensitive layer thereon, the photosensitive composition comprising;

- 5 (A) a branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear
- 10 polymer backbone segment wherein the branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer,
- 15 wherein
- (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,
- 20 (b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,
- 25 (c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and
- 30 (d) the branch polymer segment(s) contain from about 35% to 100% of the hydrophilic groups; and
- (B) at least one photoactive component;

(2) imagewise exposing the layer to actinic radiation to form exposed and unexposed areas,

5 (3) modifying exposed or unexposed areas of the layer by removing exposed or unexposed areas, depositing a material on or in the surface of the exposed or unexposed areas or treating the surface with a reactant to develop an
10 image in the exposed or unexposed areas to form an imaged layer.

46. The process of claim 45 in which the photosensitive composition is applied as a neat, solvent-free, photosensitive liquid.

15 47. The process of claim 44 in which the photosensitive composition is applied as a coating solution and dried to a solid photosensitive layer.

48. The process of claim 44 in which the photosensitive composition is applied by laminating a
20 supported solid photosensitive layer thereof.

49. The process of claim 44 in which at least a portion of the exposed or unexposed areas of the layer are removed in step (3) to form a relief image.

50. The process of claim 49 in which all of the
25 exposed or unexposed areas of the layer are removed from the substrate surface in step (3) to form stencil resist areas and complimentary, unprotected, substrate, surface areas.

51. The process of claim 50 in which after step
30 (3), the unprotected, substrate, surface areas are permanently modified by etching the substrate, surface areas or depositing a material thereon.

52. The process of claim 51 in which after the substrate surfaces are modified, the resist areas are removed from the substrate.

53. The process of claim 51 in which unprotected,
5 substrate, surface areas are modified by depositing a metal thereon by plating or soldering.

54. The process of claim 50 wherein after step (3) the resist areas are cured by heating, by uniformly exposing to actinic radiation, by treating with a
10 chemical reagent or by a combination thereof.

55. The process of claim 49 wherein the exposed or unexposed areas of the layer are removed with an alkaline or acid, aqueous developer therefor.

56. The process of claim 49 wherein the exposed or
15 unexposed areas of the layer are removed with an organic solvent developer therefor.

57. The process of claim 49 wherein the exposed or unexposed areas of the layer are peeled from the complimentary unexposed or exposed areas adhered to the
20 substrate.

58. The process of claim 44 wherein colorant or powdered material is adhered to the exposed or unexposed areas to form a visible surface image.

59. The process of claim 44 and claim 58 wherein
25 after step (3), steps (1), (2) and (3) are repeated one or more times to form a multilayered image.

60. The process of claim 56 in which the photoactive component comprises

- 30
- (a) an addition polymerizable ethylenically unsaturated monomer, and
 - (b) an initiating system activated by actinic radiation.

61. A process for forming a solder mask on a printed circuit substrate bearing on its surface, a raised, conductive circuit pattern, the process comprising the steps of:

- 5 (1) applying to the substrate surface bearing the circuit pattern, a photopolymerizable composition to form a photopolymerizable layer thereon, the photopolymerizable composition comprising;
- 10 (A) a branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the
- 15 branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer, wherein
- 20 (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,
- 25 (b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,
- 30 (c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and

- (d) the branch polymer segment(s)
contain from about 35% to 100% of
the hydrophilic groups; and
- (B) an addition polymerizable monomer
containing at least two terminal,
ethylenically unsaturated groups; and
- (C) an initiating system activated by
actinic radiation;
- (2) imagewise exposing the layer to
actinic radiation to form exposed
and unexposed areas,
- (3) removing unexposed areas of the
layer to form a stencil solder
mask image in the exposed areas
and complimentary, unprotected
areas of the circuit pattern.

62. The process of claim 61 wherein after step (3)
the resist areas are cured by heating, by uniformly
exposing to actinic radiation, by treating with a
chemical reagent or by a combination thereof.

63. The process of claim 61 wherein the
photopolymerizable composition contains a thermally
activated crosslinking component.

64. A sensitive composition comprising

- (a) a branched polymer product comprising a
plurality of branch polymer segments
chemically linked along a linear polymer
backbone segment wherein the branch
polymer segments are formed during
addition polymerization of the branched
polymer product from at least one
ethylenically unsaturated macromer
component containing one or more

- hydrophilic functional groups, wherein the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 30,000 and a polydispersity (M_w/M_n) of not greater than about 5, and
- (b) at least one photoactive or thermally active component.

65. A coating composition comprising a dispersion or solution of a branched polymer product containing hydrophilic groups comprising one or more branch polymer segment(s) chemically linked along a linear polymer backbone segment wherein the branch polymer product is formed during addition polymerization of at least one ethylenically unsaturated macromer component and at least one ethylenically unsaturated comonomer, wherein
- (a) the ethylenically unsaturated macromer component has a weight average molecular weight (M_w) of not greater than 40,000,
- (b) the linear polymer backbone segment has a weight average molecular weight (M_w) between about 10,000 and about 500,000,
- (c) the weight ratio of the linear polymer backbone segment to the branch polymer segment(s) is within a range of about 200/1 to about 1/4, and
- (d) the branch polymer segment(s) contain from about 35% to 100% of the hydrophilic groups.

66. The coating composition of claim 65 comprising a crosslinking agent.

67. A substrate coated with a dried film of a dispersion or solution of the branched polymer product of claim 65.

68. A dry film derived from a dispersion or
5 solution of the branched polymer product of claim 65.

69. A molded article derived from the branched polymer product of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/01328

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ C 08 F 265/06, C 08 F 4/80, G 03 F 7/00, G 03 F 7/26, IPC: C 09 D 151/06		
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <div style="display: flex; justify-content: space-between;"> <div style="width: 30%;">Classification System </div> <div style="width: 70%;">Classification Symbols</div> </div> <div style="border-top: 1px solid black; padding-top: 5px;"> IPC⁵ : C 08 F, C 08 L, C 09 D, C 09 J, G 03 F, H 05 K </div> <div style="border-top: 1px solid black; padding-top: 5px; font-size: small;"> Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched * </div>		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4 501 855 (NOREN) 26 February 1985 (26.02.85), see claims.	1-20, 65
Y	EP, A2, 0 357 229 (E.I. DU PONT) 07 March 1990 (07.03.90), see page 3, lines 36-56; claims 1-9.	1-23, 34
A	EP, A2, 0 280 979 (BASF) 07 September 1988 (07.09.88), see claims; columns 1,2,5-9 (cited in the application).	1-20, 24-26, 45,54, 55,61, 62
Y	US, A, 4 680 352 (JANOWICZ) 14 July 1987 (14.07.87), see column 1, lines 13-22,34, column 7, lines 32-44	1-3, 13,21- 23,65
<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>¹⁵ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>¹⁶ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search <div style="text-align: center; font-size: large;">26 June 1992</div>		Date of Mailing of this International Search Report <div style="text-align: center; font-size: large;">10 JUL 1992</div>
International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>		Signature of Authorized Officer <div style="display: flex; align-items: center;"> <div style="margin-right: 20px;">Mm N. KUIPER</div> </div>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	(cited in the application). -- US, A, 4 247 619 (COHEN) 27 January 1981 (27.01.81), see claims; column 5, line 45 - column 6, line 52 (cited in the application). ----	1-20, 24, 39- 41, 45

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 92/01328 SAE 58512

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visé ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
US A 4501855	26-02-85	keine - none - rien	
US A 4680352	14-07-87	AT E 46704 AT E 48143 CA A1 1246298 CA A1 1246795 DE C0 3665868 DE C0 3667062 EP A1 196783 EP A1 199436 EP B1 199436 EP B1 196783 JP A2 61228006 JP A2 61241302 US A 4694054 AU A1 61512/86 DK A0 3875/86 DK A 3875/86 AU B2 607121	15-10-89 15-12-89 06-12-88 13-12-88 02-11-89 28-12-89 08-10-86 29-10-86 27-09-89 23-11-89 11-10-86 27-10-86 15-09-87 18-02-88 14-08-86 28-07-87 28-02-91
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EP A2 280979	07-09-88	DE A1 3706561 EP A3 280979 EP B1 280979 JP A2 63229451 US A 5061602	08-09-88 27-09-89 03-06-92 26-09-88 29-10-91